IUPAC Partnership Develops Standards and a Data Retrieval System for Ionic Liquids

In spite of the many advantages that ionic liquids are predicted to offer as green solvents, fundamental data on their physical and chemical properties, property measurement methodology, high quality data on reference systems, standards for reporting thermodynamic data, and creation of a comprehensive database infrastructure are needed to provide US industry with a knowledge base to exploit these solvents.

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Ionic liquids, a class of organic salts that are liquid at or near room temperature, have been proposed as solvents for green processing, as seen in a variety of scientific articles including *Chemical & Engineering News*, "Ionic Liquids in Organic Synthesis" and *Chemical Engineering Progress*, "Ionic Liquids Make an Environmental Splash." To reach an international consensus on the central issues, and realize the potential of these liquids as green solvents in the shortest time possible, two International Union of Pure and Applied Chemistry (IUPAC) projects have been initiated with NIST involvement. The first of these is projects, (2002-005-1-100) *Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems* is chaired by K. N. Marsh of the University of Canterbury, New Zealand, with J. F. Brennecke, M. Frenkel, A. Heintz, J. W. Magee, L. P. N. Rebelo, and K. R. Seddon as task force members. An absence of consistent requirements for the publication of thermodynamic data for ionic liquids, has lead to major barriers to interpretation of data and a critical evaluation with regard to their uncertainties. This drastically diminishes the value of the reported numerical data for use in a variety of engineering applications. To address these issues, standardization in reporting thermodynamic data for ionic liquids could be accomplished by an expansion of the Guided Data Capture (GDC) software developed by the TRC Group. This IUPAC task group has convened for international discussion of the issues by conducting two workshops on ionic liquids, held at the 17th IUPAC Conference on Chemical Thermodynamics (ICCT) in Rostock, Germany (*J. Chem. Eng. Data* **2003**, *48*, 445) and at the 18th ICCT in Beijing, China in 2005. A Third Workshop will be convened in Boulder as part of the 19th ICCT (Thermo International 2006).

In 2005, the IUPAC Task Group initiated an international round robin study of a reference substance, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, abbreviated as [C_6mim][Tf2N]. Using NIST-supplied reagents, 1.5 kg of [C_6mim][Tf2N] was synthesized at the U. of Notre Dame and then was shipped to NIST. After drying and chemical characterization at NIST, samples were packaged under an inert atmosphere and were shipped to the participating laboratories. NIST is coordinating round robin studies of density, heat capacity, and viscosity, and is participating in measurements of those properties plus thermal conductivity and electrolytic conductivity.

Results have been reported in two articles in the *Journal of Chemical Engineering Data*, and citations are listed below.

Y.U. Paulechka, G.J. Kabo, A.V. Blokhin, O.A Vydrov, J.W. Magee, and M. Frenkel,**Thermodynamic Properties of 1-Butyl-3-methyl-imidazolium Hexafluorophosphate in the Ideal Gas State.** *J. Chem. Eng. Data* **2003**, *48*, 457-462.

G. J. Kabo, A. V. Blohkin, Y. U. Paulechka, A. G. Kabo, M. P. Shymanovich, and J. W. Magee**, Thermodynamic Properties of 1-Butyl-3-methyl-imidazolium Hexafluorophosphate in the Condensed State.** *J. Chem. Eng. Data* **2004**, *49*, 453-461.

Ionic liquids have many proposed advantages as **green solvents.** NIST is active in two IUPAC task groups that were established to overcome barriers to their exploitation for industrial applications: one deals with the standardization of data reporting, and the second involves the compilation of an distributed-access, public-domain *Ionic Liquids Database*.

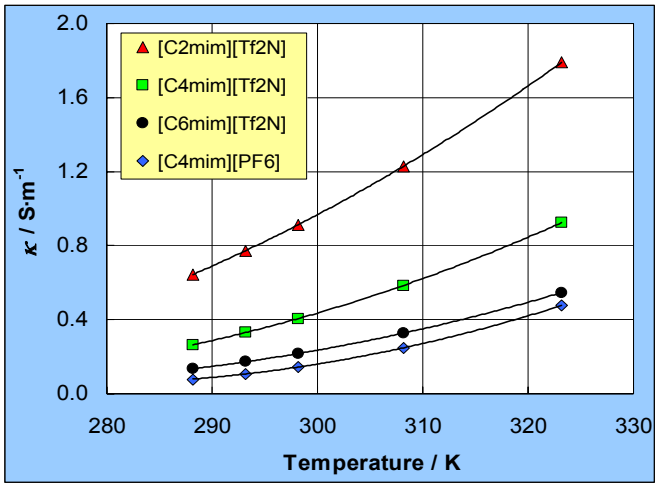
The second IUPAC project, (2003-020-2-100) *Ionic Liquids Database*, is chaired by K. R. Seddon, with A. Burgess, M. Frenkel, M. Gaune-Escard, A. Heintz, J. W. Magee, K. N. Marsh, and R. Sheldon serving as task force members. This group is addressing the need for an open-access, public-domain data storage system to contain information pertaining to ionic liquids. The vision for this project is to create a distributed-access data retrieval system for ionic liquids and their mixtures

that encompasses thermophysical and thermochemical data, chemical structure, solvent properties, ionic liquids use in synthesis, reviews, reactions and catalysis, manufacturer information, benchmark properties and models. To facilitate the storage and retrieval of ionic liquids property data, modifications that support ionic materials were applied to the TRC Group's SOURCE Database and to GDC software. By using these components, an ionic liquids database (ILThermo) was created and populated with data from a selection of published work. Task group meetings have been held in Delft, Netherlands in 2004 and Beijing, China in 2005. At both meetings, NIST's keynote presentations set the agenda for discussion. In Beijing, the task group created a plan for release of ILThermo in FY 2006.

The NIST measurement program continues to provide benchmark physical properties data for selected ionic liquids that are liquid-phase at room temperature. For example, for 1-butyl-3-methylimidazolium hexafluorophosphate, [C_4mim][PF_6], considered to be the archetypal ionic liquid, NIST published the first reports of thermodynamic properties of the ideal gas state at temperatures to 1500 K and high-accuracy thermodynamic properties in condensed states (crystal, glass, and liquid) covering a range of temperatures from 5 K to 550 K. In addition, a study of industrial gas solubilities in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C_4mim][Tf2N], was completed. Companion papers, published in FY 2005, report a seminal calorimetric study of the enthalpy of solution of an ionic liquid in H_2O.

Studies were also reported of the viscosity and the electrolytic conductivity – a key electrical characteristic of hydrophobic ionic liquids and the effect of a dilute water impurity.

The figure shows the electrolytic conductivity for four ionic liquids was measured as a function of temperature with a new conductivity cell for hygroscopic samples.



In 2005 this international research team reported a discovery that ionic liquids are vacuum distillable under specific conditions, thus opening the door to new separation processes and purification by this means.

Publications:

Physical Property Measurements and a Comprehensive Data Retrieval System for Ionic Liquids. J. W. Magee, G. J. Kabo, and M. Frenkel, in *ACS Symposium Series Ionic Liquids III: Fundamentals, Challenges and Opportunities*; R. D. Rogers and K. R. Seddon, eds.; Washington, DC: American Chemical Society (2005).

The Effect of Dissolved Water on the Viscosities of Hydrophobic Ionic Liquids. J. A. Widegren, A. Laesecke, and J. W. Magee, *Chem. Commun.* **2005**, 1610-1612.

Enthalpy of Solution of Potassium Tetrafluoroborate in Water and in Aqueous Sodium Fluoride. Thermodynamic Properties of the Aqueous Tetrafluoroborate Anion and Potassium Tetrafluoroborate. D. G. Archer, *J. Chem. Eng. Data* **2005**, *50*, 692-696.

Electrolytic Conductivity of Four Imidazolium-Based Room-Temperature Ionic Liquids and the Effect of a Water Impurity. J. A. Widegren, E.. M., Saurer, K. N., Marsh, and J. W. Magee, *J. Chem. Thermodyn.* **2005**, *37*, 569-575.

Enthalpy of Solution of 1-Octyl-3-methylimidazolium Tetrafluoroborate in Water and in Aqueous Sodium Fluoride. D. G. Archer, J. A. Widegren, D. R. Kirklin, and J. W. Magee, *J. Chem. Eng. Data* **2005**, *50*, 1484-1491.

Solubilities of Gases in the Ionic Liquid 1-Butyl-3-methylimidazolium bis (Trifluoromethylsulfonyl)amide, B.-C. Lee and S. L. Outcalt, *J. Chem. Eng. Data* **2006**, *51*, 892-897.

Publication in Nature:

Upon the Distillation and Volatility of Ionic Liquids. M. J. Earle, J. M. S. S Esperança, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, and J. A. Widegren, *Nature* **2006**, *439*, 831-834.

Future Plans: Properties studies will continue with new measurements of thermodynamic density, heat capacity, speed of sound, enthalpy of solution, gas solubility, volatility, and also expanded transport property measurements – viscosity, thermal conductivity and electrolytic conductivity. Structure-property relationships for physical properties will be explored by analyzing data in ILThermo. The first version of the ILThermo database will be released in FY 2006. The latest version of GDC software was recently disseminated to more than 700 researchers in the ionic liquids community, thus providing for an ongoing mechanism that promises to fully populate ILThermo and maintain its comprehensive coverage of thermophysical properties.